THE ACTION OF ULTRA-VIOLET LIGHT ON CERTAIN COLLOIDAL DISPERSIONS OF GOLD.

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DISSERTATION

Submitted in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in the Faculty of Pure Science of Columbia University in the City of New York.

BY

RALPH HOLCOMBE MÜLLER, B.S., M.A.

NEW YORK CITY
1925.

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Dedicated to
My Mother and Father.

ACKNOWLEDGMENT

The author wishes to express to his teacher and friend, Dr. Jacob J. Beaver, his sincere thanks for continued interest and advice throughout the course of the investigation.

He also wishes to thank the other members of the Chemistry Department, and also of the Physics Department for their co-operation and assistance.

THE ACTION OF ULTRA-VIOLET LIGHT ON CERTAIN COLLOIDAL DISPERSIONS OF GOLD.

INTRODUCTION.

The study of the effect of radiation upon colloidal dispersions of gold has been the object of numerous investigations. The earliest of these dealt with the reducing action of light upon gold salts, with the accompanying formation of a colloidal dispersion.[1, 2, 3, 4, 5, 6] The accelerating effect of light during the reduction of gold salts by various reducing agents has also been known for some time.[7, 8, 9, 10]

A comprehensive study of the significance of light in the formation and stability of colloidal gold has been made by Nordenson.[11] His paper contains a valuable survey and criticism of previous work on this problem. He investigated the effect of light upon the reduction of chlorauric acid by hydrogen peroxide. Reduction proceeds in the darkness or diffuse daylight with the formation of a coarse bluish suspension. The exposure to the radiation of a quartz mercury-vapor lamp, during the reduction, leads to the formation of stable sols. The degree of dispersion, and the color, depend upon the length of the exposure. The sols prepared in this manner were examined spectrophoto-metrically as well as with the ultra-microscope and the dependance of the properties upon time of exposure demonstrated. In addition he observed a coagulating effect of the ultra-violet light which is similar to that induced by weak electrolytes. He was convinced that the coagulation is not due to a photo-electric effect, because the result was the same with positively as well as negatively charged particles. Some exception however, must be taken with his method of reversing the charge on the gold particles. The method was that proposed by Burton[12] and also used by Svedberg[13] and consists in the addition of aluminum sulphate until the direction of migration under an electrical field is

reversed. Nordenson admits the possibility of interaction of the gold with the products of hydrolysis of the aluminum sulphate, but apparently considers the change in sign of the particle charge to be the only important result. He could detect no chemical change in the dispersion medium which would account for the coagulation by light. He offered two explanations for the phenomenon: 1. The light may cause a difference in potential between adjacent particles (Becquerel effect) leading to attraction and eventually precipitation. 2. The light may disturb the adsorption equilibrium between particle and associated ions, leading to instability, and later to coagulation.

In attempting to reproduce some of the many photochemical phenomena ascribed to gold sols, the author was impressed by strict dependance of these effects upon the previous history of the dispersion. Thus it was possible to prepare sols which were utterly indifferent to prolonged irradiation from the most powerful artificial source of ultraviolet light known. Other sols were prepared which, by the customary mode of designation, were "clear red and free from coarse particles" and yet were markedly sensitive to ultraviolet light.

The object of this investigation is to study the conditions under which sols can be prepared which will exhibit the photochemical properties ascribed to them; why certain dispersions are not sensitive to light and others are decidedly sensitive. In addition, the photochemical changes themselves are investigated as far as the available sources of ultra-violet light permit.

MATERIALS USED.

All solutions were made up in water having a specific conductivity of 1 to 2×10^{-6} mhos. The KCl employed was recrystallized three times from conductivity water and fused in a platinum dish. The gold wire and arcing apparatus were the same as described by Beans and Eastlack [14] with the addition of an electric stirrer. C.P. nitric and hydrochloric acid were used in the preparation of the chlorauric acid. Re-

distilled ether was used to prepare the solutions of phosphorous. Forty per cent. formalin was analyzed by the method of Blank and Finkenberger[15] and diluted to the desired concentration with conductivity water. Thirty per cent. hydrogen peroxide (superoxol) was analyzed by means of a solution of potassium permanganate, standardized against Bureau of Standards sodium oxalate. A fifty per cent. solution of hydrazine hydrate was analyzed [16] with the same permanganate solution, and both reagents were diluted to the desired concentration as needed. Fused C.P. potassium carbonate was made up to tenth normal concentration. Silver nitrate solution was checked gravimetrically and by the volumetric method of Mohr. The potassium carbonate solution was standardized against a solution of hydrochloric acid which had been accurately checked against the silver nitrate solution. Pure gallotannic acid was made up to one-tenth per cent. solutions as required. Eastman hydroquinone and pyrogallol and Eimer & Amend resublimed catechol and resorcin were employed without further purification.

PREPARATION OF THE GOLD SOLS.

Bredig Sols:

One liter of 0.0001 M. KCl was arced for 26 minutes at 3.8 amps. The solution was surrounded by an ice bath and the arcing interrupted occasionally to prevent an undue rise in temperature. The resulting sol was centrifuged for one hour with a force equal to 1,200 times gravity, and then siphoned into a well steamed Nonsol bottle. This sol and dilutions of it was used for most of the quantitative determinations, although more concentrated dispersions, up to saturation were investigated. A few sols that had been prepared for other purposes, in HCl, KI and KBr were also studied.

Reduction Methods:

The technique employed in making these sols was uniform with one or two exceptions. It consisted in diluting chlorauric acid, prepared from pure gold wire, to a concentration

equivalent to 0.05 gram Au° per liter. A liter of this solution was carefully neutralized with 0.1N potassium carbonate using litmus as an indicator. The reduction was carried out in a well steamed Pyrex beaker heated by an electric hot plate. The solution was stirred rapidly by an electric stirrer and the reducing agent added at a uniform rate from a microburet. Sols were prepared with the following reducing agents:

Phosphorous:

A saturated solution of yellow phosphorous in ether was diluted as required with redistilled ether, so that the necessary amount of phosphorous was contained in 1 cc. of the solution. The amount of phosphorous was calculated by assuming the reaction to be:

$$5\overset{+++}{Au} + 3\overset{0}{P} + 9H_2O \rightarrow 5\overset{0}{Au} + 3\overset{-}{PO_3} + 18\overset{+}{H}$$

The neutralized chlorauric acid was reduced at 85° C., by adding the ether solution uniformly, drop by drop. Well-washed CO_2-free air was bubbled through for a few minutes and after cooling the volume was corrected with conductivity water to one liter. These "Faraday sols" were a beautiful deep red, showing practically no Tyndall cone.

Formaldehyde:

The carefully analyzed formalin was diluted just before using, the amount being calculated from the equation:

$$2\overset{+++}{Au} + 3HCHO + 3H_2O \rightarrow 2\overset{0}{Au} + 3\overset{-}{HCOO} + 9\overset{+}{H}$$

The dilution was chosen to give the required amount of formaldehyde in one cc. of reagent. The reduction was made at 85° C. and the volume of the cooled sol adjusted as before. The formaldehyde method has been studied in detail by Zsigmondy[16] who insists that the water used must be distilled from a silver condenser, and that more than 120 cc. can not be prepared at one time. These sols were prepared with equal ease in 100 cc. and 1,000 cc. volume in water distilled once over alkaline permanganate and then redistilled through a block tin condenser (sp. cond. of 1 to 2×10^{-6} mhos.). The "superiority" of the water obtained from a silver condenser

may possibly be explained by an observation of Nordenson's,[17] i. e. that if a silver plate is boiled in very pure water a slight amount of colloidal silver is formed. The formation is accelerated by ultra-violet light. In his opinion, a small amount of silver oxide is formed which is very readily reduced to colloidal metal, especially in the light. From this it would seem that water distilled from a silver condenser contains nuclei which assist in stabilizing the gold sol. Several liters of sol, prepared as described, were used, and are still as clear and brilliant red after standing for nearly a year as when first prepared.

Tannin:

These sols were prepared according to the method of Wo. Ostwald.[18] They were deep red and showed no reflection of the incident light.

Acetylene:

One liter of distilled water was saturated with acetylene, prepared by dropping water on calcium carbide and bubbling the gas through sodium plumbite and then through copper sulphate to remove hydrogen sulphide and phosphine respectively. A saturated etherial solution of gold chloride was then added drop by drop, the solution being stirred vigorously by the electric stirrer. The sol was boiled to expel the ether and the volume correction made when cool. A clear red, but somewhat "thin" sol was obtained by this method.

Hydrogen Peroxide:

Two methods were employed with this reducing agent. In the first, the carefully analyzed superoxol was diluted, as required, to give necessary amount of H_2O_2 in one cc. of reagent. This amount was calculated from the equation:

$$2\overset{+++}{Au} + 3H_2O_2 \rightarrow 2\overset{\circ}{Au} + 6\overset{+}{H} + 3O_2$$

The reduction was carried out as before, in one liter of neutralized chlorauric acid at 85° C. with rapid stirring. After cooling the volume correction was made. In the second method, which has been studied in detail by Nordenson,[11] solutions of chlorauric acid were treated with hydrogen per-

oxide, and exposed in quartz vessels to the radiation from a quartz mercury vapor lamp. The solutions were not neutralized with potassium carbonate as in the other methods, as this leads to almost instantaneous reduction under the light, resulting in coarse dispersions. Reduction in the dark results in coarse suspensions, in no way resembling a colloidal dispersion. Exposures varying from one second to sixty seconds make progressively redder sols. This dependance of color upon time of exposure has been demonstrated spectrophotometrically by Nordenson.

Hydrazine:

The carefully analyzed hydrazine hydrate was diluted to the required concentration according to the equation:

$$4\overset{+++}{Au} + 3N_2H_4 \cdot H_2O \rightarrow 4\overset{\circ}{Au} + 3N_2 + 3H_2O + 12\overset{+}{H}$$

These sols were also prepared in neutralized chlorauric acid at 85° C. They were all red in color, with a tinge of violet however. Reduction in the cold gives the well known blue sols of Gutbier.[19]

Other Varieties of Sol:

A few dispersions were made using pyrogallol, quinol, resorcinol, catechol. The number of reducing agents that have have been used for preparing gold sols is legion. No attempt was made to exhaust all the possibilities, but rather to make a sufficient variety of sols so that the conclusions drawn from their photochemical behavior would not be restricted to a special type of dispersion.

Behavior of the Dispersions Toward Radiation.

The gold sols, prepared as described above, were exposed to the direct radiation of a quartz mercury vapor lamp. For moderate irradiation a 110 volt Cooper Hewitt quartz lamp was employed, while more intense light and the far ultraviolet was secured with the aid of a 220 volt Hanovia quartz lamp. Exposures were made in fused quartz flasks of about 250 cc. capacity. [The smaller lamp was very kindly placed at our disposal by Professor H. T. Beans, while the larger

lamp and the quartz flasks were available through the courtesy of Professor J. L. R. Morgan and Mr. R. H. Crist.] These were thoroughly cleansed before use with aqua-regia and well steamed. They were stoppered with clean new corks, care being taken that the solutions did not come in contact with them at any time during the experiment. The flasks were placed ten to twenty centimeters from the lamp and kept cool by a blast of air from an electric fan. This was the arrangement used for a qualitative survey of the properties of the various sols. More elaborate precautions were taken in the quantitative study of the light effects to be described later. The preliminary results are given in Table I.

TABLE I.

Type of Gold Sol	Short Exposure (— to 2 days)	Continued Exposure (— to 8 days)
Hydrogen Peroxide	turned blue	regained red color
Tannin	" "	" " "
Quinol	" "	" " "
Catechol	" "	" " "
Resorcinol	" "	" " "
Pyrogallol	" "	" " "
Hydrazine	no effect	no effect
Phosphorous	" "	" "
Formaldehyde	" "	" "
Acetylene	" "	" "
Bredig KCl	" "	" "
Bredig HCl	" "	" "
Bredig KI	" "	" "
Bredig KBr	" "	" "

The exposures for Table I were with the 220 volt lamp. The table brings out some very interesting facts. The Bredig sols are uniformly indifferent to the radiation and this is not strange in view of the great stability of these dispersions, particularly when prepared by the Beans and Eastlack method. It is to be noted however, that they are by no means unique in their indifference to the radiation; the phosphorous, hydrazine, formaldehyde and acetylene sols being equally insensitive.

The most important result is to be found in the behavior of those sols which did undergo a change in the light. They turned blue and resembled a sol to which an excess of electrolyte has been added. To use Nordenson's words: "The light has a slow coagulating effect which is very similar to that of a weak electrolyte." Unfortunately he did not observe that continued irradiation will peptize the unstable sol and produce a sol identical in appearance and behavior with the original. Since the color change evoked by electrolytes and by light is the same, the inference, that light will completely precipitate sols, is not unnatural. Indeed, Nordenson felt that he had disproved the possibility of peptization by light. To do so he exposed some freshly precipitated silver and also gold suspended in pure water and found no evidence of sol formation. It is evident however that this is something quite different from the peptization of a sol which is just temporarily unstable, but has all the necessary stabilizing ions present. He was dealing with metal and pure water only, and any one familiar with the work of Beans and Eastlack and the theoretical considerations of Wilson[20] on the "complex theory," will appreciate why such results were negative. The examination of more than a hundred gold sols prepared in a dozen different ways during the course of this investigation has shown: that any colloidal dispersion of gold, having associated with it the necessary stabilizing ions, or possessing in general the attributes of a stable sol, though temporarily unstable for any reason, can be peptized to a stable red sol by prolonged exposure to the ultra-violet radiation from the mercury arc.

By stability is meant the absence of coarse particles, as indicated by strong reflection of light by the sol, or by their ready removal by the natural or augmented gravitational field. To give our criterion of stability quantitative form we may adopt the one first used by D. J. Beaver,[27] which is to centrifuge the sol for one hour, with a force equivalent to 1,200 times gravity.

In other words, any sol made blue by exposure to the ultra-violet light can be restored to the original red color by

prolonged exposure. Any sol which is blue and unstable at the time of formation, due, let us say, to too rapid reduction, but similar in all other respects to a stable sol, can be changed to a red sol by prolonged exposure.

The effect is not due to heating of the dispersion, because in all cases the sols were kept at room temperature or lower. The peptization is not a spontaneous reaction for it was found that dispersions that had been made blue by exposure to the light did not regain their red color for months even in the sunlight, but required about two hundred hours exposure to the ultra-violet to effect peptization.

After peptization is effected the light seems to have no further effect. Reasons for this will be given later.

From the data given in Table I one cannot make any definite conclusions as to the reasons for photochemical sensitivity or photochemical indifference. Why, for instance, should a sol prepared with hydrogen peroxide be sensitive to light, and one prepared with formaldehyde be insensitive? It will be seen later that the conditions under which the sol is formed determine its behavior toward ultra-violet light.

The Bredig sols, which suffered no visible change under illumination, were further investigated by means of accurate conductance measurements. Apparatus was devised to permit a sol to be illuminated at constant temperature, with uniform stirring. Provision was made to determine the conductance from time to time without interrupting the exposure or removing the sol. Figure 1a, shows schematically the arrangement of the apparatus.

The gold sol to be investigated was placed in the pyrex cell (a) which was provided with a sealed-in quartz capsule (q) of cylindrical shape, having plane parallel walls. The two limbs of the cell were closed with accurately turned fibre caps, the one bearing a motor-driven stirrer (c), the other a conductivity cell of the plunge type (d). The cell and its fittings were held securely by the lid of the copper-lined box (b), and could be removed readily for cleaning and filling. Constant temperature was maintained by pumping water through the box from the thermostat (t) and the tubes (h)

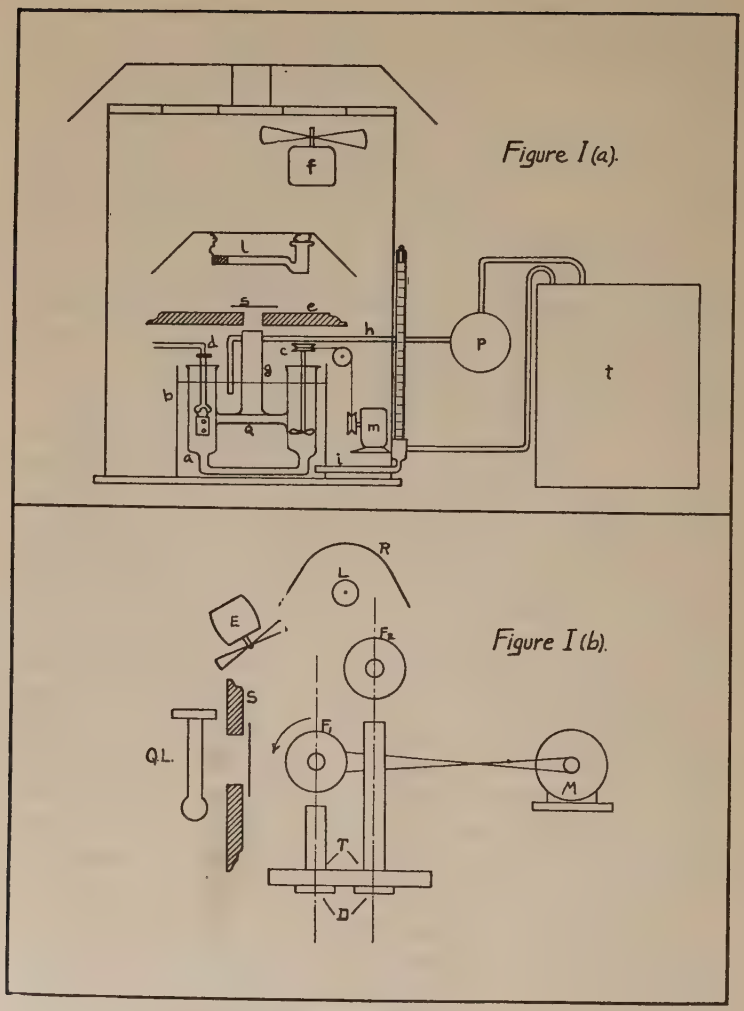


Figure I (a).

Figure I (b).

and (i). A Beckmann thermometer (r) immersed in a small well indicated the temperature of the water leaving the region of the conductivity cell. Radiation from the quartz mercury-vapor lamp (l), illuminated the sol at (q), an asbestos-board screen (e) shielding stray radiation and the shutter (s) providing control of the illumination. A glass tube (g) was

sealed to the quartz capsule (q) to act as a dam and prevent the cooling water, which is soon fouled by the pump, from covering the window and absorbing the radiation. A large ventilating fan (f), fastened to the wall of the housing which contained the entire apparatus, served to prevent undue heating of the surroundings by the lamp. The thermostat was controlled by the vacuum tube relay method of Beaver and Beaver,[21] and was maintained at 25° ± 0.001°. After several months of experimenting it was possible to maintain the temperature in the vicinity of the cell, to ± 0.005° though in warm weather it was found necessary to install an additional ventilating fan controlled automatically by a thermo-regulator.

Conductivity measurements were made with Leeds and Northrup equipment consisting of a small Vreland oscillator of 500 or 1,000 cycles per second, the higher frequency being used for these measurements; a circular slide wire bridge of the Kohlrausch type, a small resistance box, for use up to 1,000 ohms, consisting of bifilar-wound coils with three dials, and a larger box for use up to 110,000 ohms having two dials and Curtis coils. A large variable rotary air condenser of 0.005 M.F. capacity was used to balance out the capacity of the cell. All connections were soldered, and the instruments were adequately protected by grounded shields. Corrections were made for the resistance of the lead wires.

Measurements of Conductivity.

The procedure adopted in making the measurements was as follows. The mercury arc was struck at least twenty minutes before making a run, keeping the shutter (s) closed. The cell was filled with 150 cc. of the sol to be investigated and fastened in place with stirrer and conductivity cell in position. After the contents attained the proper temperature, the conductivity was measured. A slight drift in the direction of lower conductivity could not be eliminated and since the drift was found to be independent of the rate of stirring, cleaning of the cell, previous history of the electrodes, or age of the sol and was not present when the cell

was filled with pure water or with dilute solutions of crystalloids, it was concluded that the drift was due to the gradual adsorption of conducting substances associated with the colloidal dispersion. The drift was very small however and did not interfere with the measurements.

With the Bredig sols described, no difference in conductivity could be detected after opening the shutter, and periods of illumination up to 24 hours showed no difference from the conductivity in the dark. It was then decided to see if the rate of precipitation of the gold sol by means of a dilute solution of an electrolyte is affected by radiation.

Spear, Jones, Neave and Schlager[22] showed that the precipitation of colloidal platinum containing electrolytes is greatly accelerated by the action of ultra-violet light.

A polyvalent ion was chosen so that a small concentration of it would suffice to cause precipitation, and thus keep the conductivity within the same range. After preliminary trials, 0.001 M. thorium nitrate was chosen. 150 cc. of the gold sol were treated with 0.32 cc. of the 0.001 M. Th $(NO_3)_4$, which had previously been brought to 25° C. The addition was made in a pyrex beaker, with uniform stirring from an electric stirrer, the reagent being added at a rapid, but uniform rate, from a micro-buret. The sol was immediately transferred to the cell, the stirrer started, and ten minutes after the addition of the reagent, the shutter was opened and the irradiation begun. The procedure was modified from time to time, such as adding the reagent with the cell in place and illuminating instantly, but the results were the same and therefor the more convenient method described first was used in most of the runs.

The conductivity decreased rapidly indicating a change in the reaction mixture which did not manifest itself visibly until about an hour later. A plot of the conductivity against time yielded a hyperbola and therefore a plot of t/k against t gave a straight line. The slope of this line is a resistance term, which is, dimensionally, a velocity. Table II gives two representative runs and Figure 2 a plot of the results.

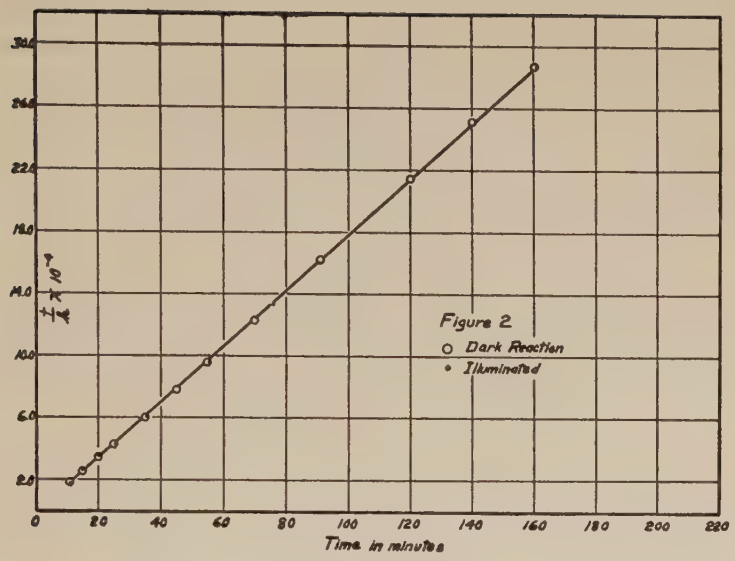


TABLE II.

Time (min.)	Dark Sp. Cond. $\times 10^5$	t/k $\times 10^{-4}$	Time (min.)	Illuminated Sp. Cond. $\times 10^5$	t/k $\times 10^{-4}$
11	5.922	1.857	11	6.087	1.807
15	5.889	2.547	16	6.045	2.647
20	5.858	3.414	21	6.014	3.492
25	5.835	4.285	26	5.987	4.343
35	5.795	6.040	36	5.939	6.061
45	5.760	7.812	56	5.851	9.571
55	5.733	9.594	76	5.779	13.15
70	5.694	12.30	161	5.621	28.64
91	5.650	17.10			
120	5.594	21.45			
140	5.567	25.15			
160	5.554	28.74			

It will be seen from Table II that the values for the conductivities at 11 minutes differ appreciably although the conditions were exactly alike. The difference is not constant however and does not represent an error in the amount of the reagent, or one introduced during the course of the meas-

urement. In the twenty-seven series of measurements made, of which the two in Table II are representative, this variation in the original conductivity was always present, and was undoubtedly due to unavoidable irregularities in the rate of adding the electrolyte. As long as the amount added was the same, the rate of precipitation was reproducible, although the initial conductivity was different, due to rapid initial adsorption, or to some other unknown cause. All factors were varied, such as concentration, intensity of the light, and also the wave length, which was accomplished by means of ray filters. In each case the conductivity curves for light and dark were identical within the limits of experimental error.

Colormetric Determination.

Another attempt was made, by an entirely different method, to demonstrate and prove the indifference of the Bredig dispersions to ultra-violet light. Direct titration of samples of sol, which had been exposed to the intense radiation in quartz flasks, with thorium nitrate, was attempted, but despite the careful temperature control and accurate color matching, the results were not reproducible enough and the method was abandoned in favor of the following. Figure 1 (b) illustratrates the arrangement of the apparatus. The dispersion to be illuminated was placed in the quartz flask (F_1), which was mounted upon a vertical shaft and rotated about 100 R.P.M. by the motor (M). It was illuminated by the quartz mercury-vapor lamp (Q.L.) 10 cm. distant, and cooled by a blast of air from the electric fan (E). A similar quartz flask (F_2) for comparison, was placed in back of, and to the right of F_1. Light from a 100 watt Mazda lamp (L) was reflected from a white surface (R) and the portion of the light coming through the two flasks entered the opaque tubes (T), falling upon the ground-glass disks (D). The board (B) supporting the tubes and glass disks was blackened. When the flasks were filled with gold sol, and illuminated from L, the disks (D) showed as brilliant red patches against the dark background. The intensities were readily adjusted by manipulation of the reflector (R).

The liminal value of thorium nitrate, necessary for the precipitation of the sol under investigation, was determined by adding 0.0001 M. $Th(NO_3)_4$ from a micro-buret to the sol at a uniform rate, the sol being stirred uniformly by an electric stirrer. A series of additions made in this manner, showed that the minimum amount, necessary to cause an immediate change to a purple color, was 0.19 c.c. A slightly smaller amount, say 0.10 c.c. would cause precipitation after some time had elapsed.

Each flask was filled with 100 cc. of the sol and F_1 set in motion. 0.10 cc. of the reagent was then added to F_1 and the shutter (S) opened. From time to time the lamp (L) was lit and the colors were compared. During the comparison the shutter (S) was closed momentarily to permit of better matching. Blank runs were checked by this method by ± 20 seconds, where the total time required was about one hour. The first change of color on the left-hand disk was taken as the end point. The transition was from red to purple and was very easy to detect. This particular concentration required 41 minutes without illumination and exactly 41 minutes in the ultra-violet light. Further trials with different concentrations of sol and precipitating electrolyte indicated the same indifference to radiation and confirmed the conclusions arrived at from the conductivity measurements.

A possible explanation for the stability of the Bredig sols toward radiation, aside from the fact that in most all other respects they are the most stable type of gold sol, is to be had from the following considerations. Since it was possible to peptize temporarily unstable sols by means of ultra-violet light, it is reasonable to assume that any slight instability in a Bredig sol could be overcome by prolonged exposure to ultra-violet light. Now the electric arc or spark under water is one of the richest sources of ultra-violet light known, particularly the condensed spark. It is very probably therefor, that the sol undergoes all the photo-chemical changes that it is capable of undergoing, including the final peptization, at the very moment of its formation, and hence such a dispersion would be inert to further irradiation. The intensity of

the radiation present in the arc is very readily demonstrated. A very small amount of quinine-hydrochloride was dissolved in water and the gold wires were arced in the solution as usual. The entire solution fluoresced brilliantly enough to read by, though the arc itself was only about a millimeter in diameter. The fluorescence was several times as intense as that caused by the mercury-vapor lamp. The ideal proof of the explanation would be to make a sol with the bulk of the solution shielded from the radiation. This presents great experimental difficulties, although Svedberg[23] has made sols with an arc enclosed in a translucent quartz tube.

The function of radiation in the formation of gold sols was not investigated in detail here, because Nordenson had shown the change in color caused by different periods of exposure. An attempt was made however to repeat some of his experiments. The rate of formation of hydrogen peroxide sols, as a function of time of exposure to ultra-violet light was followed, and agreed in general with his results, though the results could not be checked with the precision implied by his data. His reaction mixtures however, were made by adding a "few drops" of H_2O_2 to $HAuCl_4$ solutions. It soon became evident that the problem had not been sufficiently investigated from the chemical standpoint, and until the effect of amount of H_2O_2 and other factors were known, little importance could be attached to these values.

Some of these factors were investigated for the hydrogen peroxide sols and are described later.

Behavior of Photosensitive Sols.

Among those sols which had exhibited sensitivity to light in the preliminary experiments, the sols prepared by the tannin method were investigated more closely. In attempting to reproduce one of these sols, which had proven very suitable for the purpose, a sol was produced, identical in appearance, but absolutely indifferent toward radiation. It was found that slight variations in the hydrogen ion concentration of the neutralized chlorauric acid accounted for the differences after reduction with tannin.

Electrometric titrations of the chlorauric acid were therefore made at room temperature (22°-25° C.). A saturated calomel cell and hydrogen electrode were used, and the N/10 potassium carbonate was added from a micro-buret. A Leeds and Northrup portable potentiometer was employed. Duplicate titrations were made, using another calomel cell, which had been checked repeatedly against known standards, and a Leeds and Northrup Type K potentiometer. The two curves were practically identical. A curve was then plotted of ccs. K_2CO_3 against pH of the solution, for the given gold content.

Solutions were made up from this curve and after heating to the proper temperature were reduced with the tannic acid. Stirring and rate of addition of the reducing agent were uniform. The temperature was maintained to within ± 1° throughout the reduction. The time required for the appearance of the first trace of color was noted. The time values were not as reproducible as might be desired, but since so many factors are involved in the rate of reduction, this is to be expected unless unusually great precautions are taken. The values are however, accurate enough to indicate the significance of time of reduction, and its apparent relationship to the hydrogen ion concentration, and the color and stability of the dispersion.

Table III gives the results of these experiments.

TABLE III.

No.	Gm. Au°/Liter	pH	Temp.	Time of Red ± 20%	Color
1	0.025	3.16	65°	312 secs.	Grayish suspension
2	"	3.43	"	217 "	Bluish suspension
3	"	3.76	"	17 "	Purple suspension
4	"	4.16	"	16.5 "	Violet sol
5	"	4.53	"	9.3 "	Red sol
6	"	4.72	"	5 "	Red sol
7	"	7.66	"	14 "	Red sol
8	"	8.95	"	17 "	Red sol, trace of blue
9	"	9.36	"	30 "	Bluish-red sol
10	"	9.63	"	58 "	Violet sol

It will be seen from Table III that both the color and time of reduction depend upon the hydrogen ion concentration of the solution. The more stable, red sols are formed near the neutral point and are those which are most rapidly reduced. There is a greater toleration of alkali than of acid as it requires very high concentrations of alkali to yield a suspension. All of the unstable dispersions with the exception of the coarse suspensions were peptized to stable red sols by prolonged exposure to the mercury-vapor lamp. The red sols (No. 5-8) exhibited varying sensitivity toward the light, the minimum being found, by interpolation, to be in the vicinity of pH 7.0. This supports Ostwald's statement that the most stable sols by the tannin method, are those in which the chlorauric acid is made neutral to litmus. The rather wide range (pH 4.53-8.95) for the clear red sols was found to be restricted to tannin, and not typical of sols prepared by other methods, and is possibly due to a protective effect of the tannin.

The influence of alkali upon the stability of gold sols prepared by the reduction method, is mentioned in the literature, the statement being made that gold sols are more stable in alkaline solutions than in neutral or acid solutions.[24] Pihlblad,[25] who studied the effect of size of particle on the light absorption of disperse systems, measured the shift of the absorption band in gold sols, due to the addition of alkali to the reaction mixture. He showed a drift toward the violet, i. e., the tendency to form red sols upon the addition of alkali, but did not extend his measurements far enough to show that the color passes through an optimum and then becomes blue again.

It was decided to investigate this matter more accurately and therefore the hydrogen peroxide sols were chosen as they seemed to offer less complexity than the tannin sols. The color of each dispersion was determined spectrophotometrically. For this purpose a Brace spectrometer with a variable rotating sector was employed. The aperture of the sector could be varied while running and was calibrated to read from 0 to 100%. The sector was placed in front of one

collimator, and a glass cell containing the sol was placed in front of the other collimator. White light, reflected from magnesium oxide surfaces, was passed through both collimators and the two fields matched over the entire spectral range, before starting any absorption measurements. During the matching of fields, the cell was filled with distilled water and the rotating sector set at 100%. The spectrometer table was calibrated with the following spectral lines: Li, 6708 A. U.; Na, 5896, 5890 A. U.; Hg (arc), 5791, 5770, 5461, 4358, 4046 A. U. A large calibration chart was made from these values from which values of the wave length could be read.

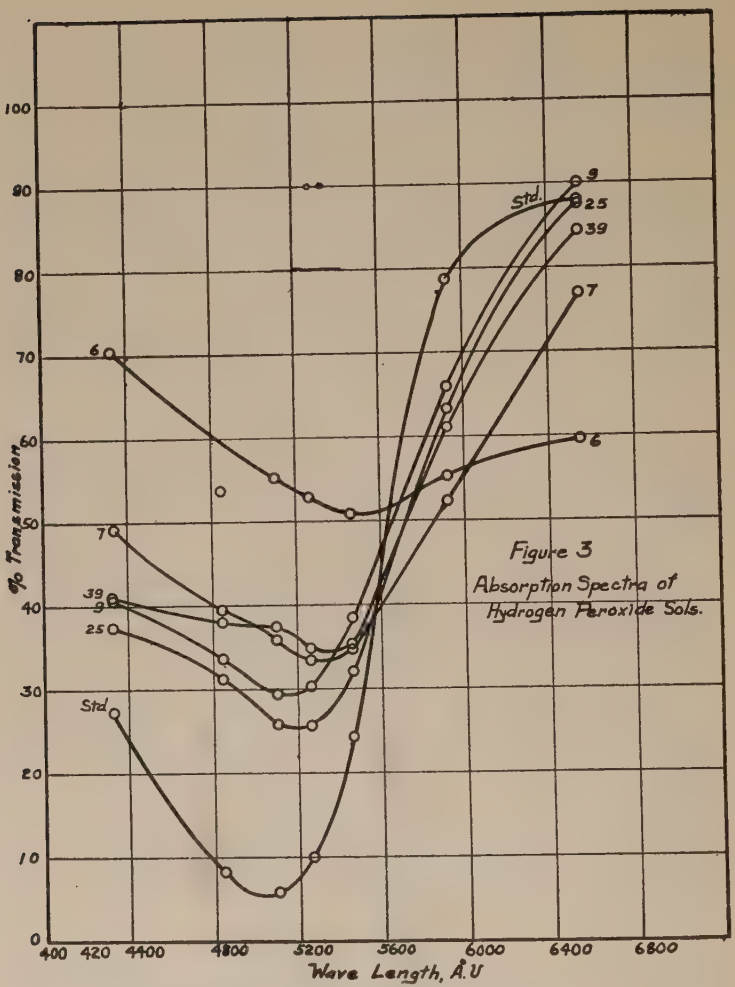
The sols were made under identical conditions and were all reduced at 85° C. The percentage transmission was determined for the following wave lengths: 4331, 4847, 5102, 5263, 5461, 5925, 6549 A. U. Each transmission value given is the average of several determinations. In the extreme red and violet ends of the spectrum it was necessary to take the average of three or four matchings since the visibility maximum lies in the green and comparison in the red and violet is very difficult and fatiguing to the eye.

Table IV gives the absorption data for sols reduced at different hydrogen ion concentrations with hydrogen peroxide. Figure 3 shows percentage transmission plotted against wave length. The last column of Table IV gives the wave length corresponding to the head of the absorption band and is obtained graphically from the absorption curves.

TABLE IV.

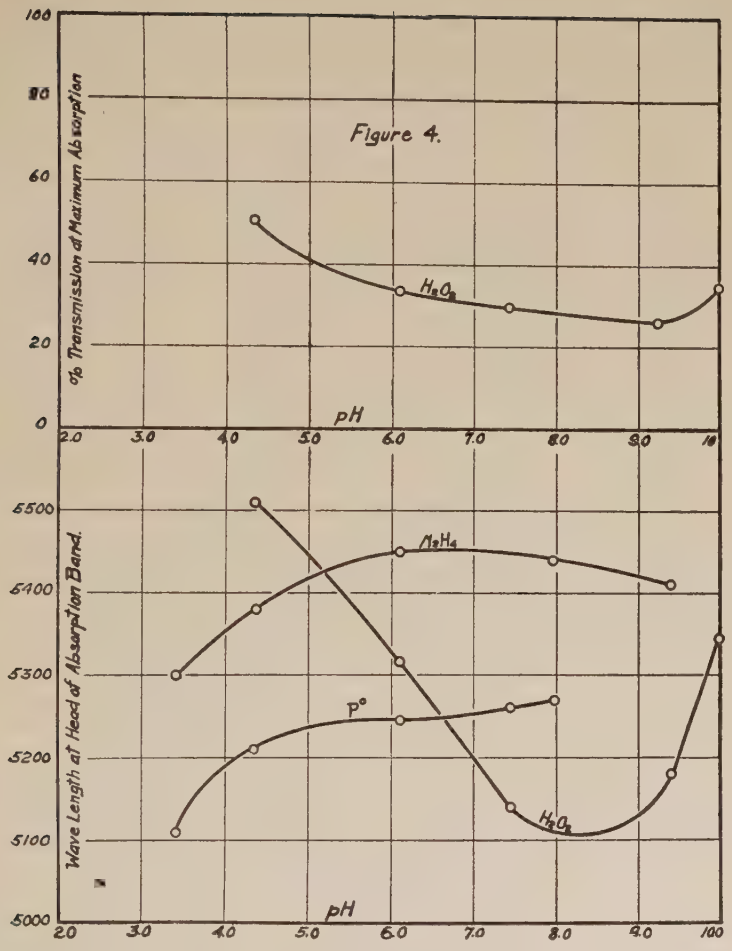
Sol No.	pH	Per Cent. Transmission for Wave Length of							Head of Abs. Band.
		4331	4847	5102	5263	5461	5925	6549	
6	4.35	70.5	53.8	55.4	53.0	51.0	55.2	59.6	5510
7	6.10	49.6	39.5	35.8	33.5	34.7	52.4	77.8	5315
9	7.45	40.6	33.6	29.3	30.2	38.5	66.0	90.0	5140
25	9.40	37.4	31.2	25.9	25.6	32.1	63.4	88.1	5180
39	10.00	41.0	38.0	37.5	34.9	35.3	61.1	84.3	5345
Color Std.		27.3	8.3	5.9	10.0	24.3	78.7	87.5	5040

The Color Standard, the absorption spectrum of which is also included in Table IV, is a convenient quantitative color refer-



ence and may also be used qualitatively in judging the color of a dispersion. The standard is used by clinicians[26] and consists of 5 c.c. of 20 per cent. by weight of cobaltous nitrate, $Co(NO_3)_2 \cdot 6H_2O$ plus 0.30 c.c. of 0.25 per cent. of potassium dichromate solution, plus 10 c.c. of water.

Figure 3 shows the progressive drift of the absorption band toward the violet end of the spectrum, and then back



toward the red end. Figure 4 shows the wave length corresponding to the maximum absorption plotted against the pH of the solution before reduction. Figure 3 affords some information about the amount of colloid formed as well as its color. It can be seen that the transmissions at the head of the absorption bands of the bluish sols No. 6 and No. 39 are quite high, indicating little absorption of the light, while for the red sols No. 9 and No. 25, the transmissions of light at

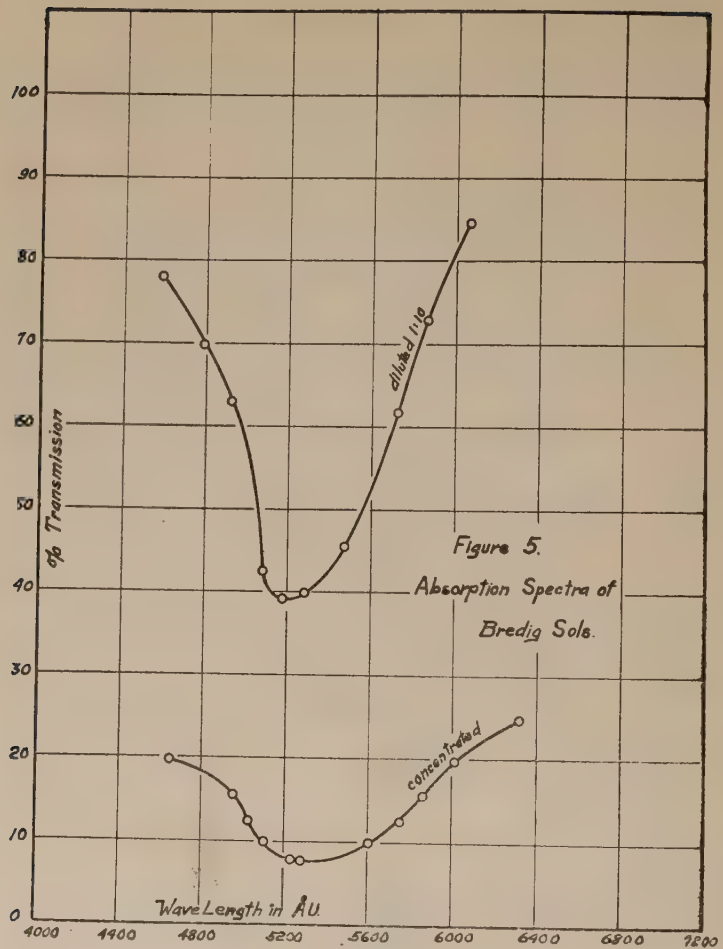


Figure 5.
Absorption Spectra of
Bredig Sols.

the heads of the bands is small, indicating great absorption. That this is really due to a difference in concentration of the disperse phase was shown by mapping the absorption of a very concentrated Bredig sol and then mapping the absorption of the same sol diluted 1:10. The maxima occur at the same wave length, but the transmissions at this wave length are 8.0% and 39.2% respectively. The difference in shape of the curves is of little importance here, since that is influenced

by reflection as well as by absorption; it is the percentage transmission at the maximum of absorption that we are concerned with. Table V and Figure 5 illustrate this point.

TABLE V.

Conc. Sol		Diluted Sol (1 : 10)	
Wave Length	% Trans.	Wave Length	% Trans.
4640 A. U.	19.8	4587 A. U.	76.1
4950	15.7	4785	69.8
5020	12.5	4933	63.1
5100	10.0	5081	42.6
5230	7.94	5180	39.4
5270	7.94	5278	40.1
5600	10.0	5475	45.7
5750	12.5	5722	61.9
5860	15.7	5869	73.0
6060	19.8	6066	84.7
6320	24.9		

The measurements on the concentrated sol were made with a Hilger Quartz Spectrograph with photometer attachment, and those on the diluted with a Lummer-Brodhun spectrophotometer and rotating sector, as the same instrument was not always available.

Returning to the hydrogen peroxide sols, it will be seen that these experiments showed that both the color and the concentration of disperse phase are influenced by the hydrogen ion concentration of the gold solution being reduced. This relationship is not as simple and general however as the above data might lead one to believe. While holding in general for the tannin sols, and quantitatively for the hydrogen peroxide sols, a similar study of dispersions made with phosphorous and hydrazine hydrate showed a continuous, but quite different variation of color with hydrogen ion concentration. Table VI gives the absorption determinations for sols prepared by the phosphorous method, and Table VII the values for sols prepared by reduction with hydrazine hydrate. All reductions were carried out at 85° C. The curves for these series are not plotted, as they are similar to the ones for hydrogen peroxide, but the dissimilarity is brought out by the plot of pH against the wave length corresponding to the

maximum of absorption, and is shown in Figure 4, along with the one for hydrogen peroxide.

TABLE VI (Phosphorous Sols).

Sol No.	pH	Per Cent. Transmission for Wave Length of							Head of Abs. Band.
		4331	4847	5102	5263	5461	5925	6549	A. U.
30	3.42	35.9	32.2	24.4	25.1	31.3	62.9	85.9	5110
33	4.35	44.2	33.1	24.5	23.8	26.7	59.5	84.5	5210
8	6.10	45.4	34.3	28.5	26.2	29.5	45.6	67.3	5245
3	7.45	37.2	34.5	29.5	27.1	30.0	48.1	68.4	5260
37	7.97	36.2	33.0	25.9	21.9	27.3	40.9	63.8	5270
Color Std.		27.3	8.3	5.9	10.0	24.3	78.7	87.5	5040

TABLE VII (Hydrazine Hydrate Sols).

Sol No.	pH	Per Cent. Transmission for Wave Length of							Head of Abs. Band.
		4331	4847	5102	5263	5461	5925	6549	A. U.
20		41.1	43.9	41.6	35.4	37.7	38.9	44.0	5300
23		32.0	38.0	37.1	33.8	33.5	40.5	53.2	5380
26		34.0	37.1	28.8	24.1	22.3	35.1	63.7	5450
29		36.3	38.3	29.0	23.0	21.7	28.8	56.3	5440
32		34.0	38.0	27.1	23.4	22.0	40.3	66.5	5410
Color Stad.		27.3	8.3	5.9	10.0	24.3	78.7	87.5	5040

An examination of these curves (Figure 4) shows immediately that the phosphorous and hydrazine hydrate sols are quite different from the hydrogen peroxide sols. In the case of phosphorous sols, the optimum conditions seem to be approached in acid solutions, below pH 4.0 and above this value are relatively uninfluenced by the hydrogen ion concentration. The same seems to be true of the hydrazine sols though the optimum is approached at both ends of the pH range. It is obvious in both cases that other factors are concerned. Chief among these is the temperature. Hydrazine sols are usually blue. At the particular temperature chosen, 85° C., and over the pH range studied, they were red, with a tinge of violet. In the case of phosphorous, better sols are usually obtained by reduction in the cold, with subsequent heating to expel the ether. These curves show then, that the given conditions are specific for the hydrogen peroxide sols. To estab-

lish all the criteria for stable sols of all types, requires a detailed study of all the factors concerned with each specific case, and is beyond the scope of the present investigation.

Photochemically, all these dispersions behaved as described above. All dispersions with a bluish or violet tinge could be peptized permanently to red sols. The sensitivity toward radiation was progressively less as neutrality was approached, and was a minimum at slight alkalinity (pH 7.5-9.0) for the peroxide sols. In this range (pH 7.5-9.0) the sensitivity though very slight, varied, so that a number of the sols, identical in appearance exhibited different behavior toward the light. All of the peroxide sols in this range would be designated as stable sols by the usual criteria of stability, so that it is evident that nothing can be predicted about the photochemical properties of a red sol from its appearance. It is only by a knowledge of the mode of preparation, such as the curve in Figure affords, that the possibility of photochemical reaction can be estimated.

The hydrogen peroxide sols were chosen for a detailed study of the photochemical properties since the general conditions for stability had been worked out and the dependance upon these conditions demonstrated. To employ red stable sols for this purpose, restricted the choice to the narrow range of hydrogen ion concentration just mentioned, which is the range in which the light sensitivity is very small. However it was imperative to use red sols in order to observe the various stages of the light change. The peptization of a blue sol represents only half of the phenomenon.

It soon became apparent that the most pronounced change in a sol upon illumination is the change in color. This change was followed by Nordenson in his experiments, but unfortunately it tells us little about the mechanism of the process. It is necessary to supplement such measurements with other tests in order to get an idea of the transformations taking place in the sol. With these sols the refractive index, conductivity, and absorption were measured and in addition conductivity titrations were made. With the intensities of ultra-violet light at present available, these effects are very

small and the utmost precision was necessary to measure them.

The reason for the small effects found was made evident by spectrograms taken in the ultra-violet with the quartz spectrograph. A fresh red sol showed complete absorption of wave lengths below 2150 A. U. The same sol made blue by radiation absorbed everything below 2070 A. U. and upon further exposure and peptization of this sol it absorbed radiation below 2010 A. U. If therefore, the radiation between 2150 and 2010 A. U. is responsible for the change from red to blue, it is evident that the peptized sol can undergo no further change, because it no longer absorbs the necessary wave lengths. From spectrograms taken for every sol investigated, it was found that the photosensitive sols absorbed the radiation below 2150 A. U. This spectral region represents but a small fraction of the total radiant energy of the quartz mercury-vapor lamp, and decreases very rapidly with the aging of the lamp. It is only with a new lamp that the far ultra-violet is available in appreciable intensity. It is for this reason that the observed effects required more than a weeks exposure.

Refractive indices were determined with a Zeiss Immersion refractometer, the cell containing the sol being immersed in a thermostat regulated at 25° C. ± 0.001°. The changes were at no time greater than five times the experimental error. A representative run made with a somewhat more sensitive tannin sol shows the magnitude of the effect.

TABLE VIII.

Time of Exposure (Hours)	Refractive Index ^{n}D ± 0.000008	Color
0	1.332658	Red with violet tinge
2	1.332674	Blue
7	1.332646	Violet
15.5	1.332619	Red-violet
26.5	1.332635	Rose Red
47	1.332638	" "
58.5	1.332635	" "
73	1.332631	" "

Table VIII shows that there is a slight but definite increase of the refractive index as the sol becomes blue which decreases again as the sol is peptized by the radiation. Each reading of the refractive index represents the average of ten settings, and is subject to an error of eight parts in the sixth place. The hydrogen peroxide sols require about 180 hours for the same changes but the magnitude is even less. Wintgen[28] showed that in a colloidal dispersion the refractive index is a linear function of the concentration and that no variation of the refractive index with degree of dispersion could be determined. Wiegner[29] also pointed out that the linear relationship holds, and could only be disturbed if varying degree of disperse phase affected the adsorption of ions present. In the above experiments, the amount of disperse phase is constant, so that the observed variations in refractive index would, according to these investigators, be ascribed to the substances adsorbed, or otherwise associated with, the colloid particle. The conductivity of the same sol under identical conditions, changes in a similar manner to the extent of about 0.3%.

For an explanation of the effect of the radiation upon the sols, it is necessary first of all, to set forth our conception of the structure of a normal gold sol, and then consider by what means radiation could modify this structure and produce the phenomena observed. Beans and Eastlack[14] have shown that anions, capable of forming stable compounds with gold, in concentrations between 0.005 and 0.00005 M. are necessary for the stability of Bredig gold sols. Such ions are present in the chemically prepared sols and the two cases are probably quite similar, indeed prolonged dialysis of a sol will eventually lead to precipitation.

Wilson[20] has extended the complex theory by applying the Donnan membrane equilibrium theory to it. According to him, the gold particle, combined in some manner, such as residual valence, with the stabilizing anion, is surrounded with a liquid layer containing cathions balancing the negative charges on the particle. The distribution of ions is different in this layer than in the bulk of the solution. Consequently

the Donnan membrane equilibrium theory can be applied. Though the ion concentration product is equal in the surface layer and the bulk of the solution, the concentration of anion and cathion is different in the surface layer, and the surface layer will have a greater total concentration than the surrounding solution. This unequal distribution of ions will give rise to a difference of potential between the enveloping film and the surrounding solution. If the concentration of ions is increased in the bulk of the solution, this difference of potential decreases and with it the stability of the dispersion.

Since no other ions enter the solution in these experiments, it can be assumed that the radiation itself disturbs the equilibrium, causing ions to move into the bulk of the solution, thus lowering the difference of potential and consequently the stability. The solution should now be blue and have a slightly greater conductivity and refractive index, due to the presence of more ions in the bulk of the solution. But as we have seen the change to a blue color is accompanied by a decrease of the absorption in the ultra-violet so that the destructive effect of the radiation can not continue without limit. A return to true equilibrium conditions then takes place with a decrease in the refractive index and conductivity and a return to the red color. The latter postulate of course implies that there are two frequencies that are effective; one which turns the sol blue and the other which turns it red. At present there is no satisfactory method of isolating narrow spectral regions of sufficient intensity to prove this point, though, as in many other photochemical reactions, this is a possible explanation.

To test this hypothesis as unequivocally as possible, the largest quartz flask available was filled with a freshly prepared peroxide sol and the following properties of the sol were determined: absorption curve, conductance, refractive index. An attempt was also made to measure the ion concentration directly by means of a conductance titration with silver nitrate, according to the method employed by D. J. Beaver.[27] All measurements were made on portions of the same sol in order to have them strictly comparable. With the

particular sol employed the blue color was attained after 18 hours exposure and the final peptization to red again after 183 hours. Table IX gives the values of the conductivity and refractive index. Table X gives the data for the absorption spectra, and Table XI the data for the conductance titrations, the plots of which are shown in Figure 6.

The values given here are to show the relationship of the values to each other for one and the same sol. Individual determinations of each property were made in number upon various sols with similar results.

TABLE IX.

Peroxide sol 0.025 gm. Au°/1. pH = 7.45 red. at 85° C.

No.	Exposure in Hours	Conductivity $\times 10^{-4}$ mhos	Refractive Index ^{n}D
2	0	1.458	1.332623
2	18	1.462	1.332650
2	183	1.458	1.332623

TABLE X.

No.	Exp. (hrs.)	Per Cent. Transmission for Wave Length of							Head of Abs. Band.
		4331	4847	5102	5263	5461	5925	6549	A. U.
2	0	38.3	33.0	25.5	25.9	32.0	65.3	89.3	5175
2	18	49.0	43.0	35.5	31.5	33.9	52.0	69.4	5290
2	183	32.6	28.3	20.9	20.1	24.4	49.4	82.0	5210

Table X brings out several important points. First, it will be seen that the absorption is at a maximum at 5175 A. U. whereas in Table IV the absorption for a sol of this pH (7.45), is given as 5140. The difference of 35 Angström Units, which is hardly a visible difference, represents the limit of reproducibility of the sols. The deviation however is remarkably small in view of the fact that the amount of sol made for these measurements was more than ten times the amount prepared for the original absorption measurements.

It will also be seen that the absorption for the peptized sol (at 5210 A. U.) did not quite return to the original value of 5175 A. U. at the end of 183 hours although the conductivity and refractive index had returned to the original values

by that time. This emphasizes again the fact that the color of the dispersion is one of the most sensitive indicators of the changes taking place.

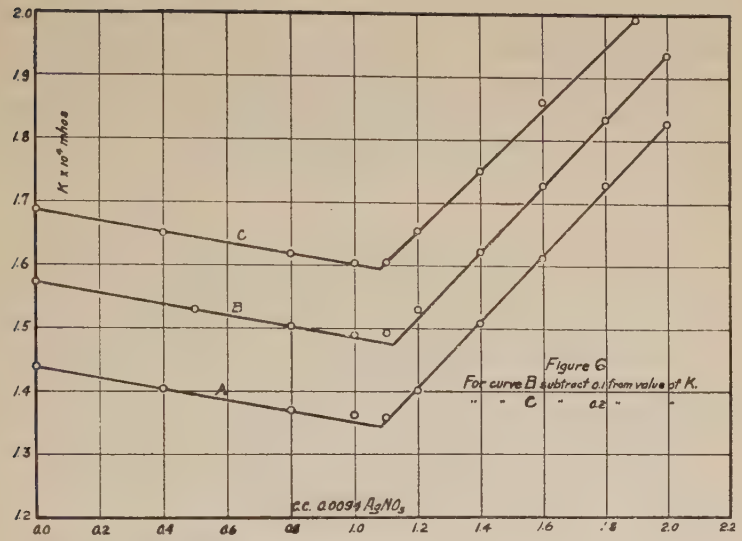
TABLE XI. CONDUCTIVITY TITRATIONS.

Sol No. 2 Titrated with 0.0094 N. $AgNO_3$ Cell Const. = 0.3820

(A) Original Sol		(B) After 18 hrs. Ex.		(C) After 183 hrs. Ex.	
c.c. $AgNO_3$	$K \times 10^{-4}$ mhos.	c.c. $AgNO_3$	$K \times 10^{-4}$ mhos.	c.c. $AgNO_3$	$K \times 10^{-4}$ mhos.
0.00	1.439	0.00	1.474	0.00	1.487
0.40	1.404	0.50	1.430	0.40	1.451
0.80	1.370	0.80	1.404	0.80	1.419
1.00	1.363	1.00	1.390	1.00	1.404
1.10	1.358	1.10	1.393	1.10	1.405
1.20	1.402	1.20	1.430	1.20	1.455
1.40	1.510	1.40	1.522	1.40	1.552
1.60	1.613	1.60	1.628	1.60	1.662
1.80	1.729	1.80	1.733	1.90	1.794
2.00	1.828	2.00	1.836		
Neutral Point = 1.080 c.c.		Neutral Point = 1.120 c.c. ± 0.002 c.c.		Neutral Point = 1.080 c.c.	

These conductivity titrations indicate an increased concentration of chloride ion in the blue sol, and a return to the original concentration in the peptized red sol. It will be observed that the initial conductivities in Table XI do not check with those in Table IX, but are slightly higher. The samples for measurement were taken from the same solution. This discrepancy was observed on several occasions and is believed to be due to the absorption of carbon dioxide from the air. The error here is not serious for a test of the foregoing hypothesis, since it is the chloride ion with which we are concerned and its determination by the conductance titration with $AgNO_3$ would not be influenced by the presence of absorbed carbon dioxide, due to the relatively higher solubility of silver carbonate.

The hypothesis outlined above required that the ionic concentration in the bulk of the solution should increase as the sol turns blue. The shift in color was shown and the in-



crease in conductance as well as the greater value for the conductance titration were also demonstrated. Prolonged exposure reduced these values again and the absorption spectra showed the return to the original color.

Though the original and final red state seem to be identical, it is evident from the photochemical indifference of the latter that they are not the same. Spectrograms in the far ultra-violet bear this out, as the peptized sol no longer absorbs the effective radiation. It is possible that when peptization is effected, the ions are more firmly associated with the complex, which would account for the greater stability toward light as well as the lack of absorption bands in the effective region of the spectrum.

Nowhere is there a greater need for a powerful source of ultra-violet light, especially monochromatic light, than in the study of such effects as we are dealing with here. In view of the peptizing ability of the radiation as herein described it should be possible, once such a source is available, to peptize sols during their formation or immediately after, and obtain dispersions with quite different properties. There are many problems involving some of the phenomena herein de-

scribed, some of them of great importance. The photographic process for example, is a photochemical problem as well as a colloidal problem, and the ultimate explanation for the mechanism will be found when the general relationship between radiation and its action on colloidal dispersions is understood.

SUMMARY.

1. The photochemical properties of gold sols depend upon the nature and method of preparation of the sols.

2. The Bredig sols are not affected by ultra-violet light, nor is the rate of precipitation of these sols by electrolytes influenced by the radiation.

3. Of the sols studied, those which are sensitive to ultra-violet light are made blue and unstable by exposure, but by prolonged irradiation are peptized to stable red sols.

4. With other factors kept constant, the color, rate of formation, and photochemical properties of chemically prepared gold sols were found to vary continuously with the hydrogen ion concentration of the reduction mixture.

5. By assuming Wilson's theory of the structure of the colloidal gold particle, and further, that light can disturb the equilibria involved, it has been shown that the ion concentrations change in accordance with the requirements of the hypothesis.

6. The necessity for a more powerful light source for this type of investigation is emphasized.

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